Organic & Supramolecular Chemistry

Kinetic Resolution of Racemic 2-Aryloxy Propionyl Chlorides Using Enantiopure (*S*)-3,4-Dihydro-3-methyl-2*H*-[1,4]benzoxazines

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Stereoselectivity in the mutual kinetic resolution (KR) of racemic 3,4-dihydro-3-methyl-2*H*-[1,4]benzoxazines and racemic 2-aryloxy propionyl chlorides was studied. Based on the results obtained, preparative methods for single enantiomers of a series of 2-aryloxy propionic acids *via* acylative KR of their racemates with enantiopure (*S*)-3,4-dihydro-3-methyl-2*H*-[1,4]benzoxazines have been proposed.

1. Introduction

Interest in developing efficient methods for preparation of enantiopure 2-aryloxy carboxylic acids is caused by their significant practical value.[1] 2-Hydroxy alkanoic acids, in particular, 2-aryloxy derivatives are the basic structures of various biologically active substances, including modern pharmaceuticals and common agrochemicals.[1a] Moreover, 2-aryloxy acids and their derivatives containing iodine in the aromatic cycle are used as chiral catalysts and reagents for various asymmetric transformations (Figure 1).[1b,c]

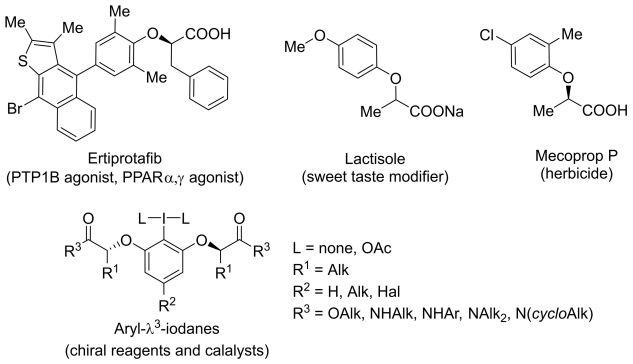

Figure 1. Selected examples of practically valuable 2-aryloxy acids and their derivatives.

Among the approaches to obtain optically pure 2-hydroxy acids, a special place is occupied by the methods of resolution of racemates. One of such classical methods is optical kinetic resolution (KR).[2] In KR, due to differences in the reaction rates of enantiomers of a racemate with a chiral non-racemic reagent or an achiral reagent in the presence of a chiral catalyst, it is possible to obtain the stereoisomerically enriched reaction product and unreacted substrate.[2] KR of racemic amines are often carried out in the course of acylation with chiral resolving agents based on optically active carboxylic acids.[2b,d,3]

We have previously studied acylative KR of racemic heterocyclic amines with chiral acid derivatives.[4] We have also performed the DFT-based simulation of the transition states in the acylation of 3-methylbenzoxazines **1a,b** (Figure 2) with 2-aryloxy acyl chlorides and suggested an explanation of the observed stereoselectivity.[4g,i] At the same time, the task of preparation of individual enantiomers of 2-arylroxy acids as a result of KR with enantiopure amines was not posed.

Herein, we report the results of studying the mutual KR of racemic 3-methylbenzoxazines and racemic 2-aryloxy propionyl chlorides in order to develop synthetic approaches to enantiopure 2-aryloxy propionic acids **2a–i** (Figure 2), including practically valuable ones, via KR using synthetically available enantiopure (*S*)-3,4-dihydro-3-methyl-2*H*-[1,4]benzoxazines **1a** and **1b**.

2. Results and Discussion

Racemic 2-substituted carboxylic acids **2a–h** were obtained starting from commercially available derivatives of 2-bromopropionic acid *via* nucleophilic substitution of bromine with appropriate phenol (thiophenol), by analogy with the literature procedures.[5] Racemic 2-(phenylsulfonyl)propionic acid (**2i**) was obtained by oxidation of acid **2h** with hydrogen peroxide as described by Kanishchev and Dolbier Jr.[6]

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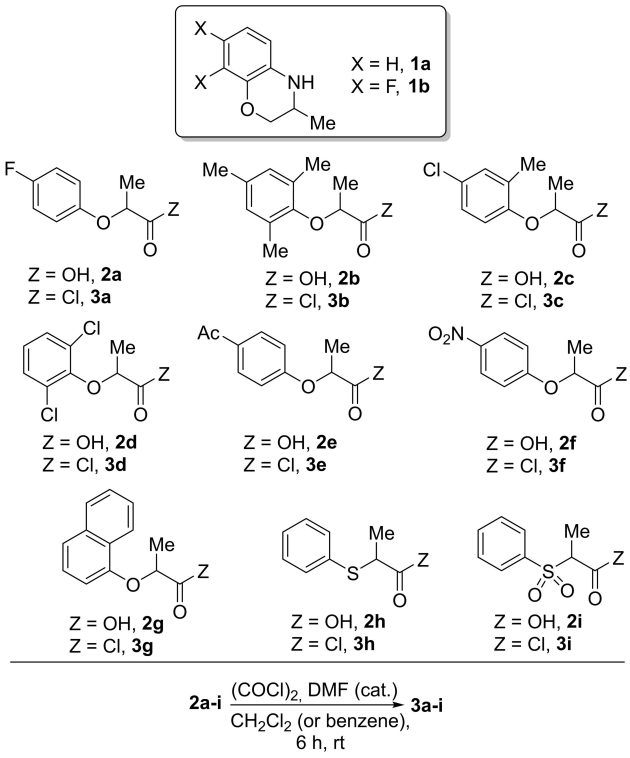
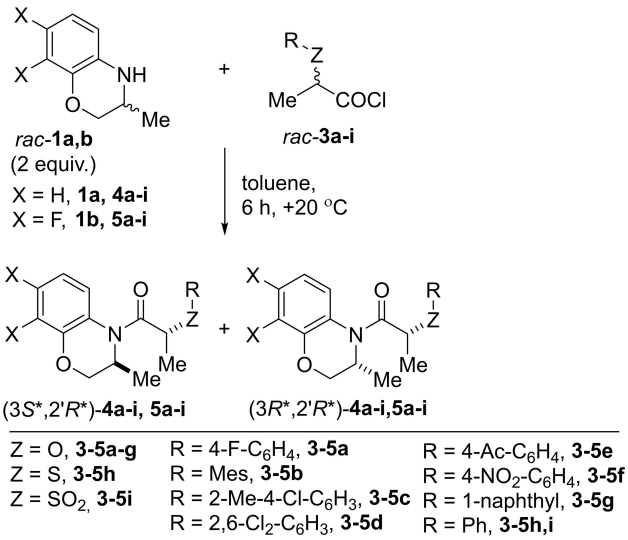


Figure 2. Structures of 3-methylbenzoxazines **1 a,b**, acids **2 a–i**, and acyl chlorides **3 a–i**.



Scheme 1. Mutual KR of amines **1 a,b** and acyl chlorides **3 a–i**.

Racemic 3-methylbenzoxazines **1 a,b** were prepared according to the known methods.[7] As for enantiopure amines (*S*)-**1 a,b**, they were obtained from racemates *via* acylative KR protocol developed by us.[8]

For carrying out acylative KR, we converted acids **2 a-i** to corresponding acyl chlorides **3 a-i** (95–100% yield) by the treatment with oxalyl chloride in dichloromethane or benzene (in the case of acyl chloride **3 b**) in the presence of catalytic amounts of DMF (Figure 2); chemical purity of compounds **3 a-i** was not less than 96% according to ^{1}H NMR spectroscopy.

At first, we determined the selectivity factor *s* of acylation of amines **1 a** and **1 b** with acyl chlorides **3 a-i**. The selectivity factor is the ratio of the rate constants of individual enantiomers ($s = k_{fast}/k_{slow}$).[2a] We used an approach based on the interaction of racemic reagents, as previously described.[4d,f,g,i] In this case, the ratio of the diastereoisomeric amides formed is equal to the selectivity factor; moreover, ratio of the starting reagents, their concentration and the reaction duration do not affect the stereochemical outcome of the process, and therefore, the *s* value can be determined quite accurately.[2a,d,9]

Racemic amines **1 a** and **1 b** were acylated at a temperature of +20 °C for 6 h; amine–acyl chloride molar ratio 2:1, initial amine concentration 0.1 M (Scheme 1). All reactions were carried out in toluene, because it has been previously demonstrated that the highest stereoselectivity in acylation of racemic heterocyclic amines with 2-aryloxy acyl chlorides is observed in this solvent.[4d] The reaction resulted in racemic (3*S**,2′*R**)- and (3*R**,2′*R**)-diastereoisomers of amides **4 a–i** and **5 a–i** with a predominance of one of the enantiomeric pairs. The diastereoisomeric ratio (*dr*) of amides **4 a–i** and **5 a–i**, which is equal to the selectivity factor *s*, was determined by GC or reversed-phase (RP) HPLC (Table 1). In each case, the major diastereoisomers were obtained in a diastereomerically pure form after recrystallization or flash column chromatography of the acylation products.

In most cases, the content of minor diastereoisomeric amide in the acylation products was rather low (up to 1.3%, see Table 1); therefore, for correct assignment of the chromato-

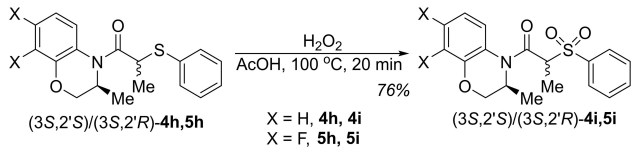
Table 1. Stereochemical results of mutual KR of racemic amines **1 a,b** and racemic acyl chlorides **3 a–i** in toluene at +20 °C.[a]

Entry	Amine	Acyl chloride	Amide, *dr* [(3*S**,2′*R**) / (3*R**,2′*R**)][b]	Selectivity factor *s*
1	**1 a**	**3 a**	**4 a**, 97.4:2.6	37
2	**1 b**	**3 a**	**5 a**, 98.3:1.7	58
3	**1 a**	**3 b**	**4 b**, 98.5:1.5	66
4	**1 b**	**3 b**	**5 b**, 98.5:1.5	66
5	**1 a**	**3 c**	**4 c**, 95.6:4.4	22
6	**1 b**	**3 c**	**5 c**, 96.0:4.0	24
7	**1 a**	**3 d**	**4 d**, 98.5:1.5	66
8	**1 b**	**3 d**	**5 d**, 98.4:1.6	62
9	**1 a**	**3 e**	**4 e**, 97.8:2.2	44
10	**1 b**	**3 e**	**5 e**, 98.7:1.3	76
11	**1 a**	**3 f**	**4 f**, 98.6:1.4[c]	70
12	**1 b**	**3 f**	**5 f**, 98.0:2.0[c]	49
13	**1 a**	**3 g**	**4 g**, 10.2:89.8	9[d]
14	**1 b**	**3 g**	**5 g**, 5.8:94.2	16[d]
15	**1 a**	**3 h**	**4 h**, 94.9:5.1	19
16	**1 b**	**3 h**	**5 h**, 97.9:2.1	47
17	**1 a**	**3 i**	**4 i**, 91.2:8.8[e]	10
18	**1 b**	**3 i**	**5 i**, 91.0:9.0[e]	10

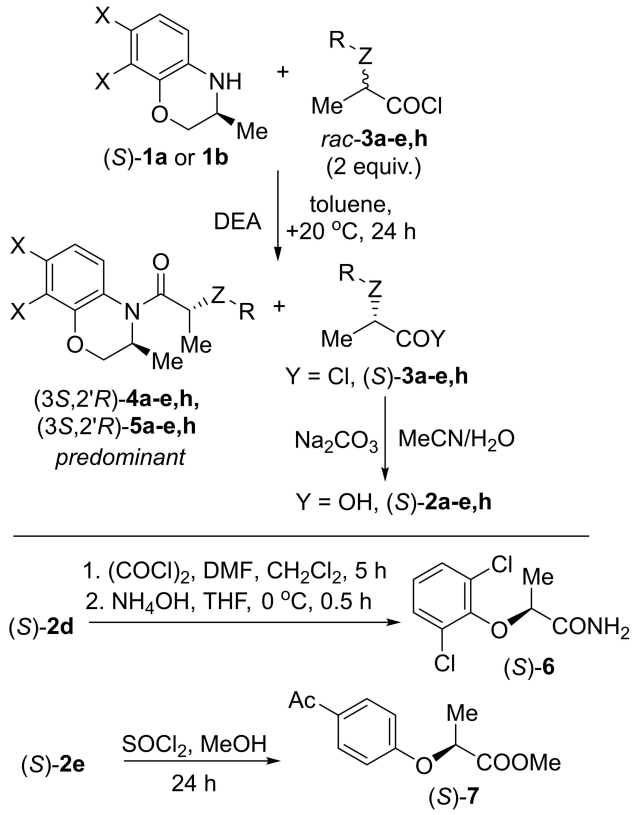
[a] Average values for 2–6 parallel runs are presented. [b] Determined by GC (see Experimental). [c] See ref.[4g] [d] $s = (3R^*,2'R^*) / (3S^*,2'R^*)$. [e] Determined by RP HPLC (see Experimental).

graphic peaks in GC, we synthesized equimolar mixtures of diastereoisomeric amides (3*S*,2′*R*)- and (3*S*,2′*S*)-**4**-**5 a–e,h** starting from enantiopure amines (*S*)-**1 a** or (*S*)-**1 b** and racemic acyl chlorides **3 a–e,h** taken in stoichiometric amounts in the presence of *N,N*-diethylaniline (DEA) as an HCl acceptor. The (3*S*,2′*R*)/(3*S*,2′*S*) mixtures of amides **4 i** and **5 i** were synthesized by oxidation of amides **4 h** and **5 h** with hydrogen peroxide under heating in acetic acid (Scheme 2) followed by flash column chromatographic purification.

To assign the configuration of amides **4 a–e,h** and **5 a–e,h**, the enantiopure amines (*S*)-**1 a** and (*S*)-**1 b** were acylated with 2 equiv. of the corresponding acyl chlorides in the presence of DEA as an HCl acceptor (Scheme 3). In this case, the maximum possible conversion (*C*, %) of the starting acyl chloride was 50%, and KR of acylating agent occurred. So, the reaction resulted in diastereoisomerically enriched (3*S*,2′*R*)-amides **4 a–e,h** and **5 a-e,h** and unreacted enantiomerically enriched acyl chlorides **3 a–e,h** that were subjected to alkaline hydrolysis



Scheme 2. Synthesis of diastereoisomeric amides (3*S*,2′*R*)/(3*S*,2′*S*)-**4,5 i**.



Scheme 3. KR of racemic acyl chlorides **3 a–e,h** with (*S*)-amines **1 a** and **1 b** for assignment of configuration.

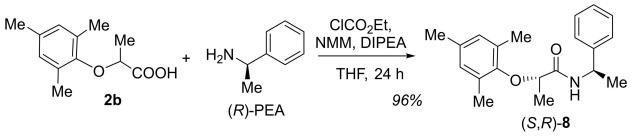
under mild conditions to isolate corresponding acids **2 a–e,h**. Comparison of the sign of optical rotation of acids **2 a–c,h** with the literature data[10] made it possible to conclude that these acids, and, consequently, unreacted acyl chlorides **3 a-c,h** were enriched with (*S*)-enantiomers. The enantiomeric composition of acids **2 d** and **2 e** was determined after conversion to the corresponding amide **6**[11] and methyl ester **7**,[12] respectively, (Scheme 3) and comparing the sign of optical rotation with published data.

We have previously found that the interaction of amines **1 a** and **1 b** with 2-(1-naphthyloxy)propionyl chloride **3 g** leads to the predominant formation of (3*R**,2′*R**)-amides **4 g** and **5 g**, respectively;[4i] while acylation of these amines with 2-(4-nitrophenyloxy)propionyl chloride **3 f** leads to the (3*S**,2′*R**)-diastereoisomers of amides **4,5 f** as the major products.[4g]

Configuration of chiral centers in the major diastereoisomers of amides **4 i** and **5 i** was determined by comparing GC of mixtures of diastereoisomers of these amides with GC data for individual diastereoisomers **4 i** and **5 i** obtained from (3*R**,2′*R**)-amides **4 h** and **5 h** (see Scheme 1).

To the best of our knowledge, enantiomers of acid **2 b** were not described in the literature; therefore, we performed preparative chiral HPLC separation of racemic acid **2 b** (Chiralcel OD–H column). Then, we carried out coupling of the fast-eluted enantiomer of compound **2 b** and (*R*)-phenylethylamine ((*R*)-PEA) in the presence of ethyl chloroformate and auxiliary bases *N*-methylmorpholine (NMM) and *N,N*-diisopropylethylamine (DIPEA) to afford amide **8** (Scheme 4). X-Ray diffraction of amide **8** (Figure 3) made it possible to determine the (*S*)-configuration of the acyl fragment from the known (*R*)-configuration of the amine fragment.

That is, (*S*)-acid **2 b** is the fast eluted enantiomer. The assignment of chromatographic peaks of enantiomers of acid **2 b** revealed that the (*S*)-isomer predominated in the acid derived from unreacted acyl chloride **3 b**. Therefore, the acylation products **4 a–e,h** and **5 a–e,h** (Scheme 3) were



Scheme 4. Synthesis of amide (*S,R*)-**8**.

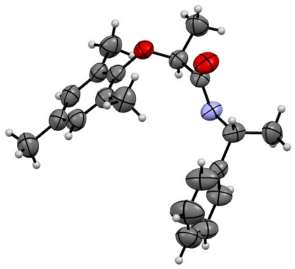
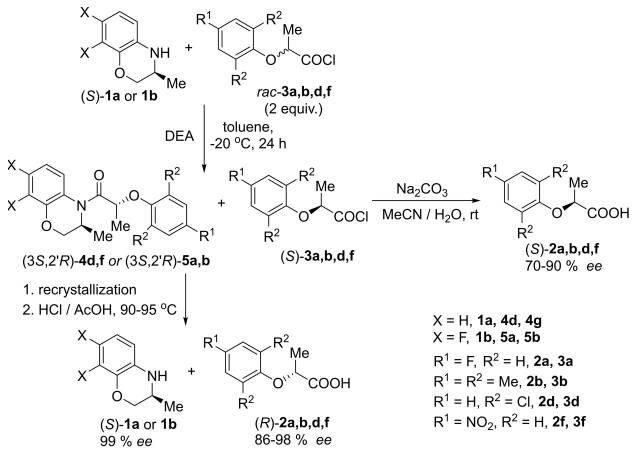


Figure 3. Structure of amide (*S,R*)-**8** (thermal ellipsoids of 50% probability).

enriched with (3*S*,2′*R*)-diastereoisomers; and the products of mutual KR (Scheme 1), with corresponding (3*S**,2′*R**)-amides.

The acylation of racemic benzoxazine **1 a** proceeded most stereoselectively when acyl chlorides **3 b**, **3 d**, and **3 f** were used as acylating agents (Table 1, entries 3, 7, and 11: selectivity factor $s = 66$, 66, and 70, respectively). Racemic 7,8-difluorobenzoxazine **1 b** most selectively reacted with reagent **3 e** (Table 1, entry 10: $s = 76$); acylation of this amine with acyl chlorides **3 a,b,d** ($s = 58$–66) proceeded with a slightly lower stereoselectivity. At the same time, the acylation of both amines **1 a** and **1 b** with racemic 2-(phenylsulfonyl)propionyl chloride (**3 i**) proceeded with low stereoselectivity (Table 1, entries 17 and 18: $s = 10$ in both cases).

Noteworthy that the "reverse" stereoselectivity (or stereoinversion) was observed when amines **1 a** and **1 b** were acylated with 2-(1-naphthyloxy)propionyl chloride (**3 g**). In this case, the products of acylation were enriched with (3*R**,2′*R**)-diastereoisomers of amides **4 g** and **5 g**, the selectivity of this process being low (Table 1, entries 13 and 14: $s = 9$ and 16). We have previously observed this phenomenon when acylation of amines **1 a,b** was carried out in dichloromethane at −20 °C.[4i]



Scheme 5. Preparation of enantiomers of acids **2 a,b,d,f** *via* KR of racemic acyl chlorides **3 a,b,d,f** with (*S*)-amines **1 a** and **1 b**.

Table 2. Stereochemical results of KR of racemic acyl chlorides **3 a,b,d,f** with amines (*S*)-**1 a,b** and subsequent preparation of (*R*)-acids **2 a,b,d,f**.

Entry	(*S*)-Amine	Acyl chloride	(3*S*,2′*R*)-Amide *de*, %[a]	Isolated yield, %[b]	(*R*)-Acid *ee*, %[c]	Isolated yield, %
1	**1 b** (X = F)	**3 a**	**5 a**, > 99	64	**2 a**, 97	84
2	**1 b** (X = F)	**3 b**	**5 b**, > 99	71	**2 b**, 97	60
3	**1 a** (X = H)	**3 d**	**4 d**, 91	91	**2 d**, 86	74
4	**1 a** (X = H)	**3 f**	**4 f**, 99	62	**2 f**, 98	76

[a] Determined by GC (for details, see Experimental). [b] After recrystallization from appropriate solvent (for details, see Experimental). [c] Determined by chiral HPLC (see Experimental).

Thus, to develop synthetic approaches for enantiopure 2-aryloxy propionic acids we chose a series of acyl chlorides, namely acyl chlorides **3 a,b,d,f**, the reactions of which with amines **1 a,b** proceeded with a relatively high stereoselectivity (selectivity factor *s* was up to 70).

KR of racemic acyl chlorides **3 a,b,d,f** under the action of enantiopure (*S*)-amines **1 a** and **1 b** (99% *ee*) was carried out according to the method we used to assign the configuration of the synthesized amides (see Scheme 3), except that the acylation was carried out at −20 °C, since lowering the reaction temperature, as we showed earlier,[4a–e,g] leads to better stereochemical results. For KR of racemic acyl chlorides **3 a** and **3 b**, we used fluorinated amine (*S*)-**1 b**; for KR of compounds **3 d** and **3 f**, benzoxazine (*S*)-**1 a** (Scheme 5, Table 2).

Interaction of (*S*)-benzoxazine **1 b** with racemic acyl chlorides **3 a,b** (2 equiv.) resulted in diastereoisomerically enriched amides (3*S*,2′*R*)-**5 a** and (3*S*,2′*R*)-**5 b** with a diastereoisomeric excess (*de*) of 85 and 86%, respectively, and unreacted acyl chlorides (*S*)-**3 a,b** (Scheme 5). The only recrystallization of amides led to individual (3*S*,2′*R*)-diastereoisomers **5 a,b** (> 99% *de*). Configuration of amide (3*S*,2′*R*)-**5 a** was additionally confirmed by X-ray diffraction (Figure 4).

Alkaline hydrolysis of unreacted acyl chlorides (*S*)-**3 a,b** under mild conditions led to enantiomerically enriched (*S*)-acids **2 a** and **2 b** with 79 and 70% *ee*, respectively (according to chiral HPLC) (Scheme 5).

Amides (3*S*,2′*R*)-**5 a** and **5 b** were subjected to acidic hydrolysis under heating in a HCl/AcOH mixture to afford the corresponding (*R*)-acids **2 a,b** and amine (*S*)-**1 a** (99% *ee*). Based on the chiral HPLC data, we have found that the hydrolysis of diastereoisomerically pure amides (3*S*,2′*R*)-**5 a** and (3*S*,2′*R*)-**5 b** is accompanied by a slight racemization of the acyl fragment (Table 2, entries 1 and 2: **2 a**, 97% *ee*; **2 b**, 97% *ee*). The total yield of (*R*)-acids **2 a** and **2 b** was 26 and 19% (relative to the starting racemate), respectively.

In a similar manner, acylation of enantiopure benzoxazine (*S*)-**1 a** with 2 equiv. of racemic acyl chlorides **3 d** and **3 f** resulted in diastereoisomerically enriched amides (3*S*,2′*R*)-**4 d** (91% *de*) and (3*S*,2′*R*)-**4 f** (90% *de*) and unreacted enantioenriched (*S*)-acyl chlorides that were converted in acids (*S*)-**2 d** (90% *ee*) and (*S*)-**2 f** (88% *ee*) (Scheme 5). As a result of recrystallization, amide (3*S*,2′*R*)-**4 f** was obtained in diastereoisomerically pure form (99% *de*); at the same time, we failed to increase *de* of amide (3*S*,2′*R*)-**4 d** either by flash column chromatography or by preparative HPLC.

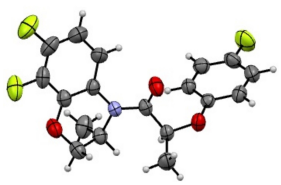


Figure 4. Structure of amide (3*S*,2′*R*)-**5 a** (thermal ellipsoids of 50% probability).

Subsequent acidic hydrolysis of amides (3*S*,2′*R*)-**4d** (91% *de*) and (3*S*,2′*R*)-**4f** (99% *de*) led to acids (*R*)-**2d** (86% *ee*) and (*R*)-**2f** (98% *ee*) and amine (*S*)-**1a** (99% *ee*). The total yield of acids (*R*)-**2d** and (*R*)-**2f** was 34 and 22%, respectively.

3. Conclusion

Thus, we studied the stereochemical results of mutual KR of racemic 3-methylbenzoxazines and acyl chlorides of a series of 2-aryloxy (2-arylthio) propionic acids. Based on these results, we proposed preparative methods for both enantiomers of 2-(4-fluorophenoxy)-, 2-(mesityloxy)-, 2-(2,6-dichlorophenoxy)-, and 2-(4-nitrophenoxy)propionic acids with an enantiomeric excess from 70 to 98%. An advantage of our approach is the possibility of regeneration of chiral resolving agents, namely (*S*)-3,4-dihydro-3-methyl-2*H*-[1,4]benzoxazines.

Supporting Information Summary

Compound characterization data can be found in the supplementary information for this article. ^{1}H, ^{19}F, and ^{13}C NMR spectra are provided in the SI, as well as GC and HPLC chromatograms.

The X-ray diffraction data, including atomic coordinates, geometric parameters, and structural factors, were deposited with the Cambridge Crystallographic Data Center (CCDC 1962953 and 1962968). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Acylation · Acyl chlorides · Benzoxazines · Kinetic resolution · Stereoselectivity

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